

## OXYNITRIDE GLASS FIBERS

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## ABSTRACT

Research at the Army Materials Technology Laboratory (AMTL) and elsewhere has shown that many glass properties including elastic modulus, hardness, and corrosion resistance are improved markedly by the substitution of nitrogen for oxygen in the glass structure. Oxynitride glasses therefore offer exciting opportunities for making high modulus, high strength glass fibers. Discussed in this paper are processes for making oxynitride glasses and fibers of glass compositions similar to commercial oxide glasses, but with considerably enhanced properties. We have made glasses with elastic moduli as high as 140 GPa (20 Msi) and fibers with moduli of 120 GPa (17 Msi) and tensile strengths up to 2900 MPa (420 ksi). AMTL holds a U.S. patent on oxynitride glass fibers, and this presentation discusses a unique process for drawing for drawing small diameter (10  $\mu$ m) oxynitride glass fibers at high drawing rates (1500 m/min). Fibers are drawn through a nozzle from molten glass in a molybdenum crucible at 1550°C. The crucible is situated in a furnace chamber in flowing nitrogen, and the fiber is wound in air outside of the chamber, making the process straightforward and commercially feasible. Strengths have been considerably improved by improving glass quality to minimize internal defects. Though the fiber strengths have been comparable with oxide fibers, work is currently in progress to further improve the elastic modulus and strength of the fibers. The high elastic modulus of oxynitride glasses indicate their potential for making fibers with tensile strengths surpassing any oxide glass fibers, and we hope to realize that potential in the near future.

## INTRODUCTION

The incorporation of nitrogen into an oxide glass network has been shown to improve several properties of the glass. Increasing nitrogen content leads to increases in glass transition temperature, viscosity, density, hardness, corrosion resistance, and elastic modulus.<sup>1</sup> For applications of high-performance resin matrix composites, the elastic modulus and strength need to be as high as possible and the density as low as possible. Presently, the continuous fibers used for advanced composites have been s-glass and e-glass fibers. S-glass fibers are from the Mg-Si-Al-O system while e-glass fibers have a Ca-Si-Al-O system. Work done at the U.S. Army Materials Technology Laboratory has focused on the processing of bulk oxynitride glass that are analogous to the s-glass composition for the purpose of drawing the glass into small diameter, high strength, high elastic modulus fibers for use in high-performance resin matrix composites. Bulk glasses have been produced with elastic modulus values of up to 140 GPa. Earlier research at MTL as shown that the fibers retain all the properties of the bulk glass.

The oxynitride glass fiber program first focused on oxynitride glasses that had improved properties over oxide glasses. Once the bulk glasses were produced, they were attempted to be drawn into fibers. The criteria for the glass was to have high modulus, low density, and be fiberized easily. The third factor is the crucial one. Bulk oxynitride glasses with superior properties have been produced at M.T.L. However, drawing thin glass fibers from these compositions has not always been easy. It is this qualifying factor that determines which compositions can be studied. After further investigation, two glass compositions were chosen for examination. Both had compositions similar to commercial s-glass. However, one had 2.72 atomic percent nitrogen and the other had 4.13 atomic percent nitrogen. These fibers had moduli that were greater than the oxide glass fibers. High modulus is the most important criteria for composites and it is in this aspect that the oxynitride glass fibers are superior. However, the tensile strengths of the oxynitride glass fibers were too low, especially when considering their potential. The effort was then put through to

improve the tensile strength of the fibers. The following paper describes that process and the accomplishments made in the fiber properties.

#### PROCEDURE

##### Glass:

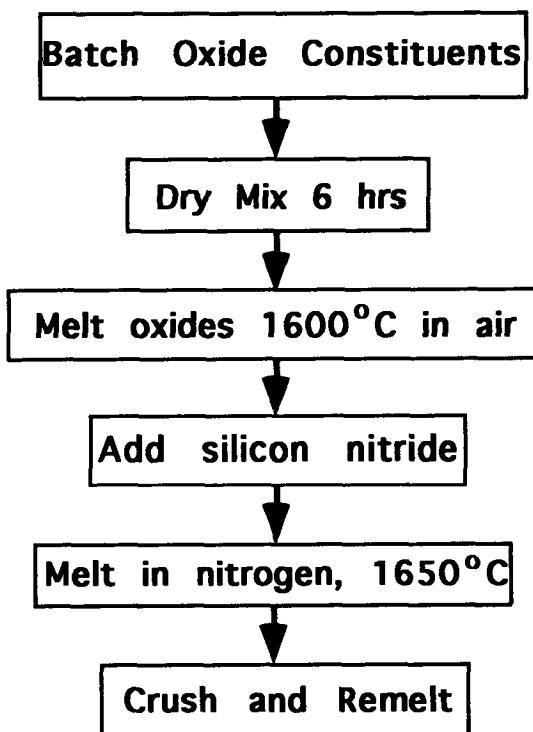
Batches were prepared using the compositions listed in Table I. To optimize the processing of the glasses, two base compositions were used so that comparison would be possible. As shown, one composition, NS8, was a  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Si}_3\text{N}_4$  composition. This glass contains 2.72 mole % nitrogen incorporated into the glass network. The other glass composition, NS 7.5, had 4.13 mole % nitrogen of the same batch materials. These two compositions were used for their good drawing characteristics thus allowing the optimization of the processing of high strength fibers.

**Table I: Oxynitride Glass Base Composition**

<b><u>Species</u></b>	<b>NS8 (2.71 at. % N) Wt. Percent</b>	<b>NS7.5 (4.13 at. % N) Wt. Percent</b>
<b>MgO</b>	<b>10.13</b>	<b>10.20</b>
<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>25.34</b>	<b>25.51</b>
<b>SiO<sub>2</sub></b>	<b>59.79</b>	<b>57.13</b>
<b>Si<sub>3</sub>N<sub>4</sub></b>	<b>4.74</b>	<b>7.16</b>

Figure I outlines the process that has been developed for the oxynitride glasses. The oxide constituent of the glasses ( $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ) were dry mixed for six hours. Wet mixing with acetone was found undesirable due to iron contamination of the acetone. The oxides were melted in air at 1600°C for two hours and quenched in water. The oxide glass was then mixed with silicon nitride (Union Carbide # 1929) and placed in a molybdenum foil crucible. The crucible was placed into a alumina crucible and loaded into a water-cooled, tungsten-mesh resistance furnace. The sample was melted at 1650°C in nitrogen at a dwell time of 2 hours and a subsequent furnace quench of 50°C per minute. The sample was removed, crushed, and remelted at the identical thermal cycle used for the first melt. At this point, the glass was ready to be characterized and drawn into fibers.

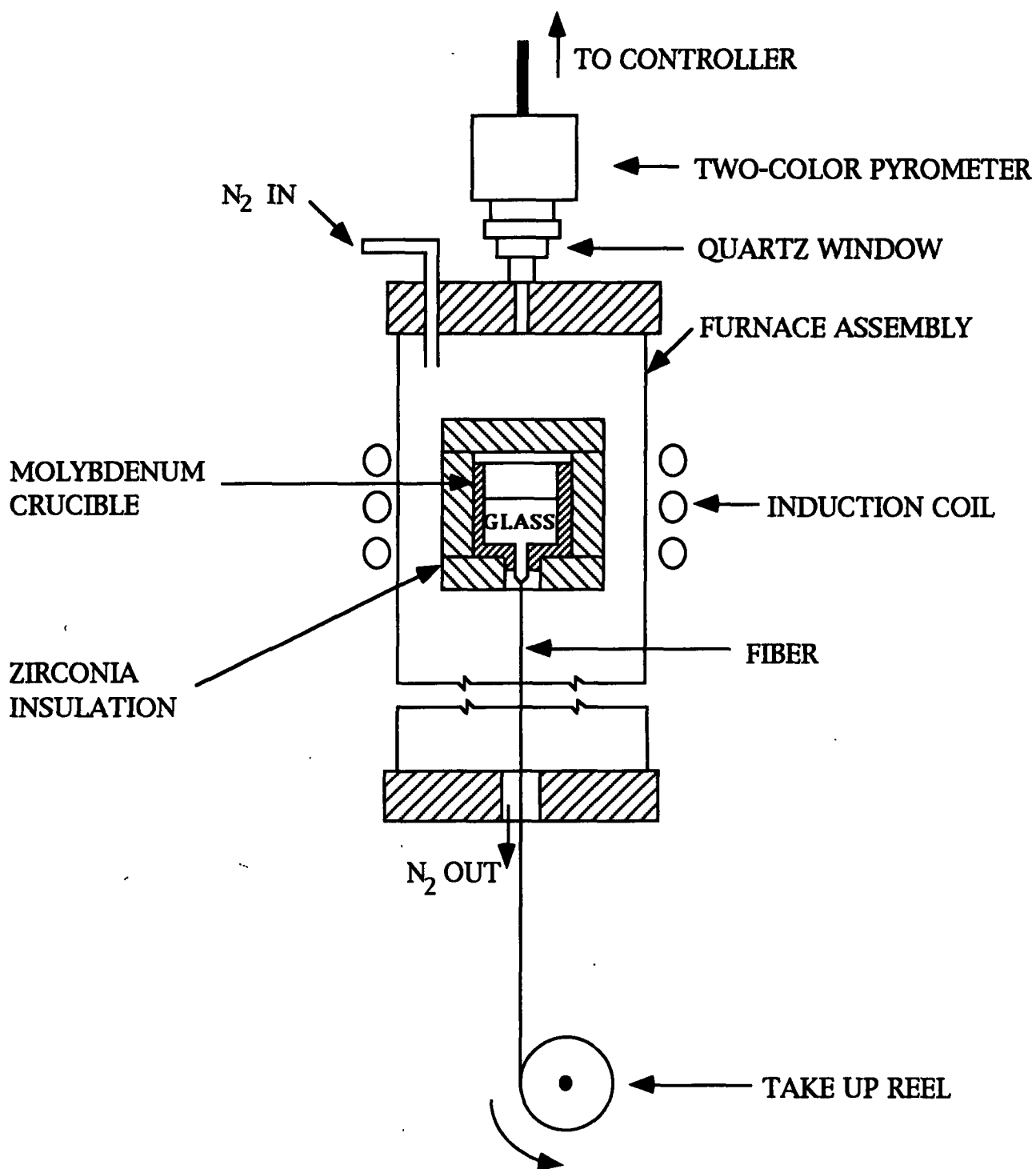
**Figure I: Oxynitride Glass Fabrication Process**



### Fibers

Once the glass was produced, it was ready to be drawn into fibers. The fiber drawing process used is very similar to commercial processing of continuous glass fibers. Figure II is a schematic representation of the fiber drawing process. The glass is placed in a molybdenum single nozzle crucible. The furnace assembly is located in a furnace chamber with flowing nitrogen. After ample time for the nitrogen flow to fill the tube the furnace is inductively heated to 1500°C- 1600°C, depending on composition. Once the temperature has stabilized, a nut is removed from the bottom fixture of the silica glass tube. A thin alumina rod is then fed through to the bushing where a glob of glass has accumulated at the nozzle. The glass adheres to the cooler alumina rod allowing the glass to thin out into a fiber as the alumina rod is pulled through the bottom of the hole. The fiber is broken off the rod and pulled manually to the winder where it is taped on. As one can see from Figure II, only the glass is exposed to the nitrogen atmosphere. The fiber is pulled in air. This design allows the process to be straightforward and commercially feasible. The winder motor speed is increased until it reaches a speed of 2400 r.p.m. or a draw rate of 1500 meters per minute. The fiber diameter, at this speed, is roughly between 8 and 12 microns. The only limitation for the fiber diameter is the drum winder speed. Presently, 2400 r.p.m. is the maximum speed of the winder. At this point, the fiber can be drawn continuously until the glass supply has diminished. However, for the purpose of characterization of the fibers, the draw is interrupted several times for sampling.

**Figure II: Schematic Representation of Oxynitride  
Glass Fiber-Drawing System**



## Characterization

Prior to the fiber draw, the bulk glass was characterized using optical techniques. The glass was observed through a microscope with transmitted light to determine the presence of any crystalline material or unmelted batch. If the glass was determined to be of good quality, the glass would draw into fibers. The density of the glass was also calculated using Archimede's method. Microhardness was also measured on polished sections using a Knoop indenter and a .98 N load.

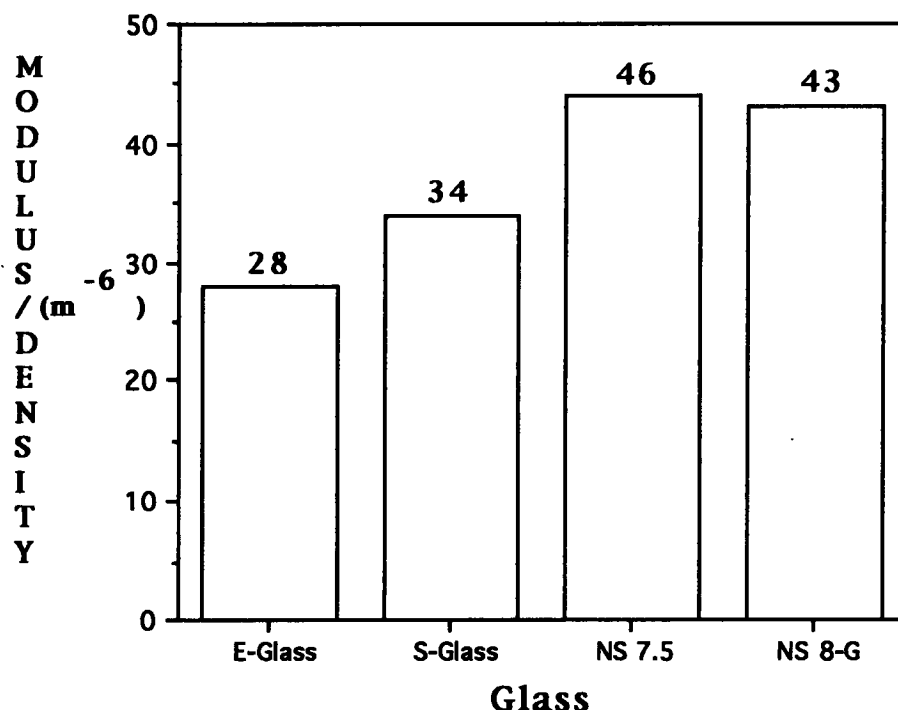
During the draw of the fibers, the fiber is broken several times for testing. Sampling is a crucial step in the characterization of the glass fibers. The fibers that are drawn do not have any sizing or any protective coating on them due to the experimental nature of the work. They are thus easily damaged and great care must be taken in their handling. The small diameters of the fibers further increased the difficulty in handling. The fibers were pulled off the line of the draw once the proper draw speed had been attained. The fibers were taped onto an I-shaped holder. A tape of seven fiber mounts with a gage length of 30 mm were placed behind the fiber. The fiber was taped to the mounts leaving the fiber within the slot untouched. Once all the fibers have been mounted, they were cemented at ends of the cut out slots. After the cement had dried, the mounts were cut off the tape and broken in tension. The fibers were broken at a crosshead speed of 1 mm per minute. The diameter of the fibers and the force required to break the fibers were recorded for future calculation of the tensile strength. Once the fibers were broken, if the fiber did not shatter, the fracture surface was studied using a S.E.M. Surface fracture analysis was performed on all fiber draws to determine the fracture origin of the fiber. In addition to the fiber tensile strength, the elastic modulus of the fibers was also determined via a sonic modulus instrument that measured the speed of sound through the fibers.

## **RESULTS**

As cited before, oxynitride glasses show considerable potential for advance composites. There is a marked improvement in the properties over oxide glass fiber counterparts. However, the tensile strength was relatively weak. One focus of work at the Materials Technology Laboratory was to produce the highest modulus, highest strength, lowest density oxynitride glass fibers possible. Using the procedure described earlier, great strides have been made in attaining that goal.

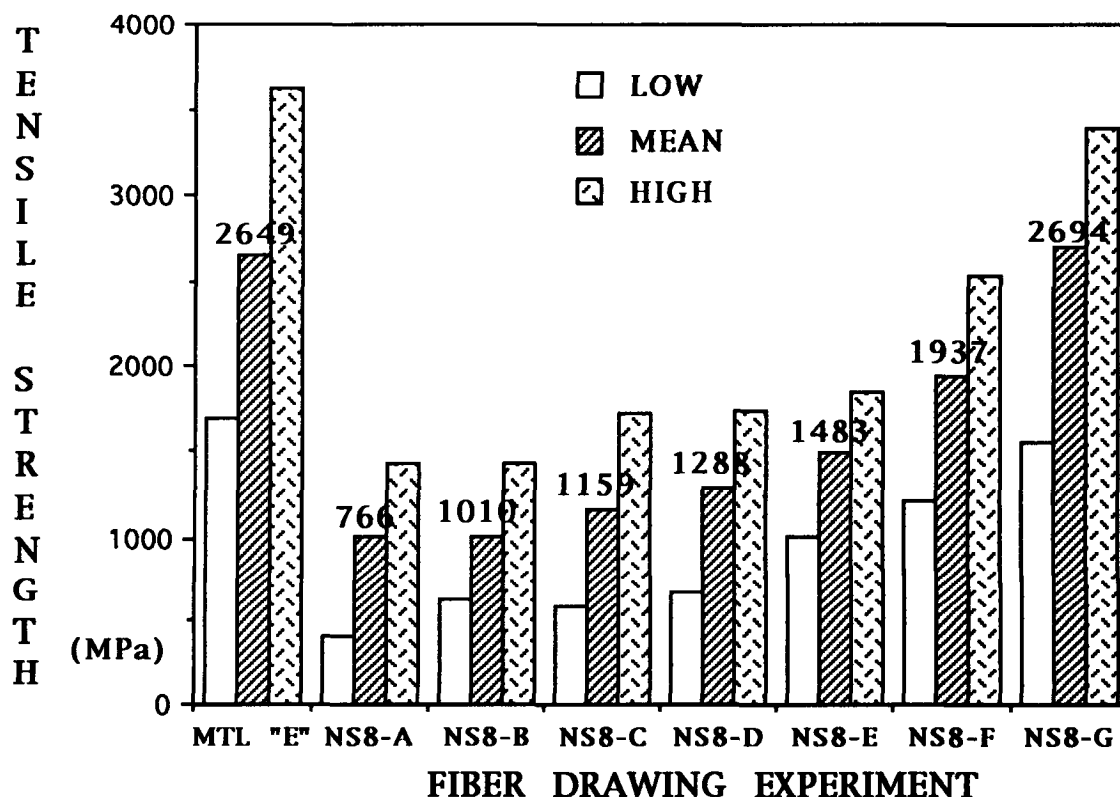
One of the important properties of the oxynitride glasses is the high elastic modulus, an important property necessary for advanced structural resin matrix composites. For aerospace application, the fibers also need to be of the lowest possible density. The modulus of the commercial e-glass with a density of  $2570 \text{ kg/m}^3$  is  $73 \text{ GPa}$ .<sup>2</sup> The density and modulus of s-glass is  $2480 \text{ kg/m}^3$  and  $85 \text{ GPa}$ , respectively. An NS8 glass has been found to have a modulus of  $105 \text{ GPa}$  with a density of  $2500 \text{ kg/m}^3$ . The NS7.5 glass, with more nitrogen, has a modulus of  $112 \text{ GPa}$ . Further examination into additives has led to glasses with modulus values of  $120 \text{ GPa}$  at a density of  $2700 \text{ kg/m}^3$ . Due to the importance of density, one convention of looking at the modulus is the Elastic Modulus to Density Ratio ( $E/\rho$ ). As seen on Figure III, the glasses made at M.T.L. have shown an improvement over conventional oxide glasses. The e-glass and s-glass had ratios of  $28 \text{ m}^{-6}$  and  $34 \text{ m}^{-6}$ , respectively. The oxynitride glass fibers displayed higher ratios. The NS 7.5 has a modulus to density ratio of  $46 \text{ m}^{-6}$ . NS8-G has an elastic modulus of modulus/density ratio of  $43 \text{ m}^{-6}$  compared to  $28 \text{ m}^{-6}$  of e glass and  $34 \text{ m}^{-6}$  of s glass. This glass also had tensile strengths comparable to oxide glass fibers.

**Figure III: Modulus/Density Comparison**



The tensile strength for the fiber is dependent on the composition as well as the processing. The base compositions, NS 8 and NS 7.5, were utilized for their good drawing properties and elastic moduli. Processing of the glass was maximized using these glass compositions. Figure IV illustrates the fiber tensile strength increases incurred due to the process changes implemented. As the process improvements have been made, the tensile strengths have become greater and greater. The MTL "E" glass refers to commercial e-glass marbles that were acquired from PPG Industries. These marbles were drawn in our fiber drawing apparatus as a standard of the fiber drawing and fiber testing techniques. The fibers tested a mean of 2649 MPa which were 15 to 20 percent weaker than industry standard. This is due to handling of the glass fibers. The tensile strength goal for the oxynitride glass fibers was to reach the strengths of commercial e-glass. The best attempt has been the NS 8-G glass fiber whose strength surpassed the MTL "E" with a mean strength of 2694 MPa. The highest tested value for the NS 8-G batch was 3320 MPa. This composition, as previously mentioned, had an elastic modulus of 121 GPa with a density of  $2700 \text{ kg/m}^3$ . This indicates the potential of higher strengths from tighter processing control. It is the first oxynitride glass fibers drawn at AMTL that couples the previous high modulus values with high tensile strength indicating the real potential for use in high performance resin matrix composites.

**Figure IV:Mg-Si-Al-O-N Glass Fiber Strength  
Increases via Process Improvements**



**Future Work:**

The oxynitride glass fibers produced thus far have already surpassed the oxide fibers with respect to elastic modulus and specific modulus. They have shown the potential for higher tensile strengths than their oxide counterparts. However, the high elastic modulus of the oxynitride glasses can still be further increased with incorporation of higher levels of nitrogen. Concurrently, the potential for higher strengths can also be improved via further process improvements. The goal is to determine the highest elastic modulus glass fibers producible with low density and high tensile strength and subsequently produce composite materials using the fibers.

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